

We thank the reviewer for your helpful comments. We largely agree with your constructive advice, and have carefully revised our manuscript. In the following, the detailed response to your comments is listed. All changes in revised manuscript have been marked with green color. In the responses below, responses are marked in purple color. And the corresponding content in revised manuscript still is shown in green in these responses.

Author Responses to Anonymous Referee #1 (RC1)

Using quantum chemical calculations combined with high level ab initio method; the authors studied the catalytic ability of the most common dicarboxylic acid in the atmosphere - oxalic acid - for the hydration reaction of SO₃. Further, taking the real atmosphere into consideration, they found that oxalic acid-catalyzed hydration reaction can compete with the water-catalyzed reaction in the upper troposphere, which has certain significance for the formation of H₂SO₄ in the atmosphere. The work is performed with care and I believe it can be published after the following concerns are fully addressed.

Reply: We appreciate the reviewer for your comments and advice. We have revised the manuscript on the basis of your comments and advice. The detail replies are described below.

Major comments:

1. In previous paper (Hazra et al, J. Am. Chem. Soc. 2011, 133, 17444), hydrolysis of SO₃ catalyzed by formic acid in the gas phase has been studied and the result shows a near barrierless mechanism for sulfuric acid formation. Moreover, we note that formic acid is considered to be the most abundant carboxylic acid, ubiquitous in the atmosphere (Millet et al. Atmos. Chem. Phys., 2015, 15, 6283; Bannan et al. J. Geophys. Res. - Atmos, 2017, 122, 488). Thus, to make this story more interesting, I think the authors should highlight the specific characteristic of oxalic acid compared with formic acid, and add more discussion about the advantages of oxalic acid acting as a catalyst.

Reply: Thank you for your advice. Oxalic acid, as the prevalent dicarboxylic acid, really has some specific characteristic compared with formic acid. The studies have shown that dicarboxylic acid can enhance nucleation in two directions compared with monocarboxylic acid. Thus, in the oxalic

acid-catalyzed SO₃ hydration reaction, the post-reactive complex (PC) still has a free carboxylic group. The PC has the potential to continue to catalyze SO₃ hydration by the free carboxylic group. In addition, the result of the manuscript shows that the PC is stable with respect to the isolate oxalic acid conformers and H₂SO₄. Thus, the PC also has the potential to promote nucleation.

We also added more discussion about the advantages of oxalic acid acting as a catalyst. In this revised manuscript, we compared the catalytic effect of oxalic acid with the nitric acid, sulfuric acid, formic acid, ammonia.

The added contents are shown in revised manuscript with the marked green color. We also put these contents below:

In Introduction section, page 3, line 9 - 11: Opposite to monocarboxylic acids, dicarboxylic acids such as oxalic acid has been proved to enhance nucleation in two directions because of its two acid moieties (Xu and Zhang, 2012).

Page 9, the last paragraph: In addition, compared to formic acid (Millet et al., 2015; Bannan et al., 2017), the SO₃ hydration reaction catalyzed by oxalic acid display some specific characteristics. Both acids can obviously decrease the energy barrier of the hydration reaction. But because oxalic acid is a dicarboxylic acid, only one in the carboxylic groups participates in the hydration reaction, and the other is free. This characteristic indicates that post-reactive complexes (PC_{Tt} and PC_{Tc}) can serve as a catalyst to continue to promote the SO₃ hydration. For these post-reactive complexes (PC_{cTb}, PC_{Ttb}, PC_{Tct} and PC_{cCt}), the above result has shown that these complexes are stable compared to the isolate H₂SO₄ and oxalic acid conformers. The free carboxylic group in these complexes can also provide the interaction site when these complexes interact with other species. The free carboxylic group of these stable post-reactive complexes indicates that these complexes have the potential to participate in nucleation.

Page 10 - 11, line 21 - 23 (page 10) and line 1 - 7 (page 11): As seen from Table2, at 298.15 K, the oxalic acid-catalyzed SO₃ hydration reaction is 10³ - 10⁵ faster than the corresponding water-catalyzed reaction (k_{cTt}/k_{w1} : 1.53×10^3 ; k_{Tt1}/k_{w1} : 5.50×10^4 ; k_{Tct1}/k_{w1} : 9.70×10^4 ; k_{cCt1}/k_{w1} : 3.31×10^5). In order to evaluate the catalytic effect of oxalic acid, we also list the rate constant ratio between other species and water catalyzed SO₃ hydration reaction. At 298 K, the nitric acid catalyzed rate constant is just 1.19 times larger than water catalyzed rate constant (Long et al., 2013). When sulfuric acid functions as an autocatalyst, the value of rate constant ratio is around 10² (Torrent-Sucarrat et al., 2012). When the formic acid acts as a catalyst, its rate constant is 10⁴ greater than that of water-catalyzed SO₃

hydration (Hazra and Sinha, 2011). The rate constant for ammonia catalyzed SO_3 hydration is 7 orders of magnitude larger than that for water catalyzed rate constant at 298 K (Bandyopadhyay et al., 2017). These results indicate that the catalytic effect of oxalic acid in SO_3 hydration reaction is better than nitric acid and sulfuric acid, and similar to formic acid, but weaker than ammonia.

2. For method and basis set of the single point energy, the CCSD(T) method with the 6-311++G(3df,3pd) is not a good match, I think it is available using at least cc-pVTZ level. If the author prefer the 6-311++G(3df,3pd) basis set when using CCSD(T) to perform the single point energy, please give the corresponding reasons.

Reply: Thank you for your comment and advice. We have recalculated the single point energy at CCSD(T)/cc-pV(T+d)Z level. As the influence of single point energy is overall, the potential energy profile and the rate constant are changed after using the new theoretic level (CCSD(T)/cc-pV(T+d)Z). For potential energy, we do not mark the changed data in the manuscript because all data are changed. Although the changed data are not marked in the revised manuscript, old and new figures are put below for showing the change:

The old Figure 1:

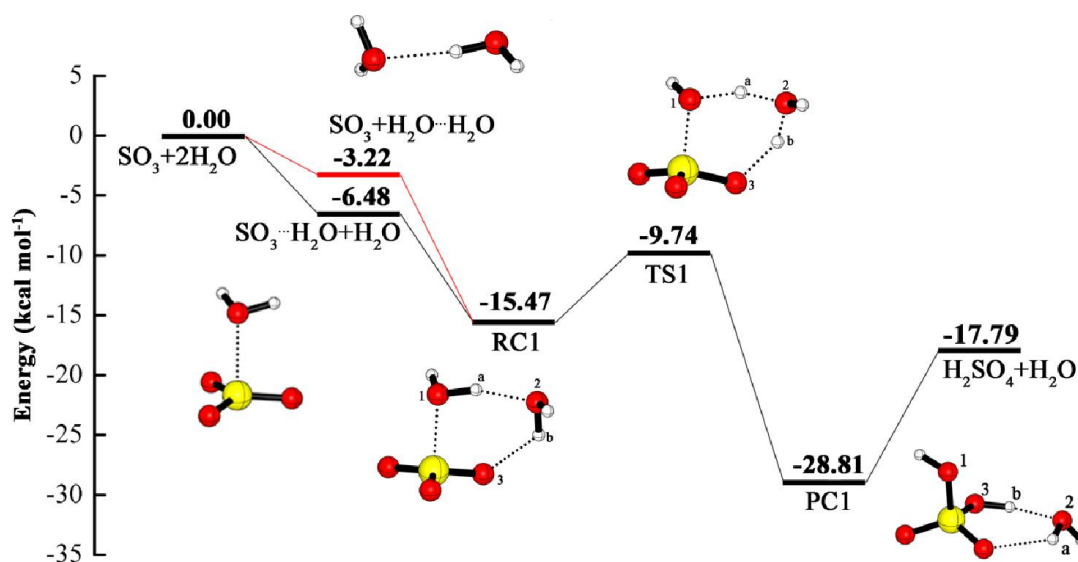


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd) level.

The new Figure 1:

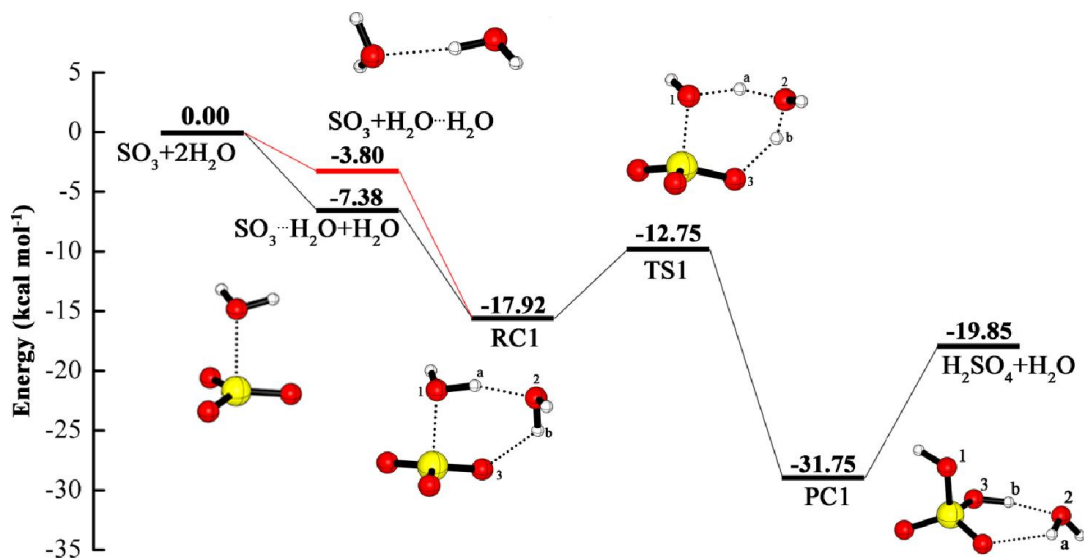
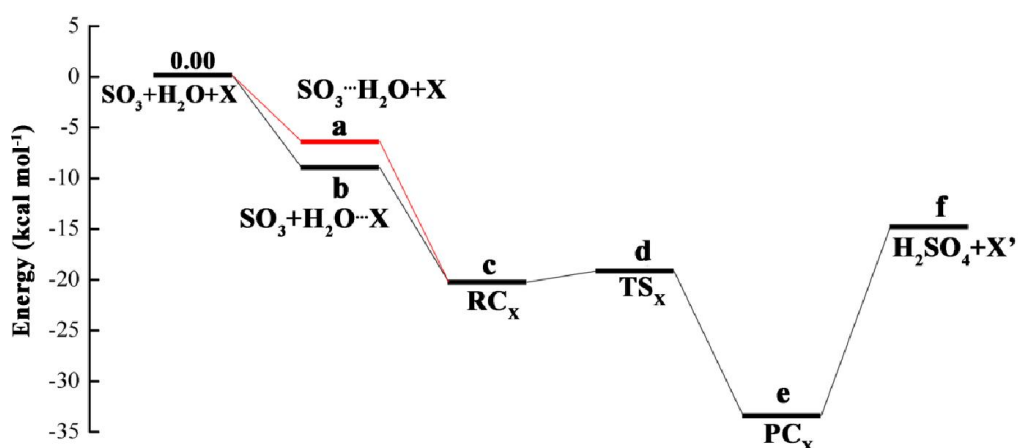


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level.

The old Figure 3:



When X = cTt,

$$a = -6.48 \quad b = -9.05 \quad c = -20.29 \quad d = -18.92 \quad e = -33.40 \quad f = -14.86 \quad (X' = \text{cCt})$$

When X = tTt,

$$a = -6.48 \quad b = -8.76 \quad c = -21.58 \quad d = -21.14 \quad e = -35.33 \quad f = -17.27 \quad (X' = \text{tCt})$$

When X = tCt,

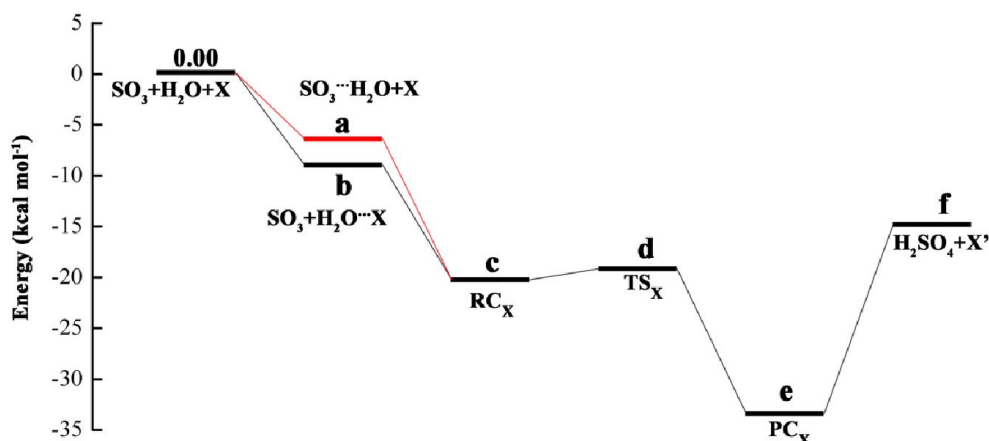
$$a = -6.48 \quad b = -8.93 \quad c = -22.04 \quad d = -21.76 \quad e = -36.05 \quad f = -18.32 \quad (X' = \text{tTt})$$

When X = cCt,

$$a = -6.48 \quad b = -9.92 \quad c = -22.53 \quad d = -22.27 \quad e = -37.60 \quad f = -20.73 \quad (X' = \text{cTt})$$

Figure 3. Calculated potential energy profile for the hydration of SO_3 with oxalic acid conformers (cTt, tTt, tCt and cCt) as catalysts at the CCSD(T)/6-311++G(3df,3pd) //M06-2X/6-311++G(3df,3pd) level.

The new Figure 3:



When X = cTt,

a = -7.38 b = -10.25 c = -21.20 d = -20.01 e = -34.52 f = -16.74 (X'=cCt)

When X = tTt,

a = -7.38 b = -9.92 c = -22.51 d = -22.27 e = -36.56 f = -19.22 (X'=tCt)

When X = tCt,

a = -7.38 b = -10.09 c = -23.01 d = -22.96 e = -37.45 f = -20.47 (X'=tTt)

When X = cCt,

a = -7.38 b = -11.10 c = -23.48 d = -23.49 e = -39.10 f = -22.95 (X'=cTt)

Figure 3. Calculated potential energy profile for the hydration of SO₃ with oxalic acid conformers (cTt, tTt, tCt and cCt) as catalysts at the CCSD(T)/cc-pV(T+d)Z //M06-2X/6-311++G(3df,3pd) level.

For the kinetics analysis, to make the rate constant more meaningful, we adjusted the entrance for rate constant calculation from SO₃ + H₂O...H₂O (or SO₃...H₂O + H₂O) and SO₃ + H₂O...OA (or SO₃...OA + H₂O) to SO₃ + H₂O + H₂O and SO₃ + H₂O + OA. And the adjustment will not affect the result of the rate comparison. The adjustment caused the great changes for Table 1, which lists the rate constant. Using the new level of theory to calculate the single point energy, it can be found from the old and new Table 5 that the relative rate decreases from 6.78 to around 0.1 at 12 km altitude. It still indicates that the oxalic acid can play a significant role in enhancing SO₃ hydration to H₂SO₄. The correspond content in revised manuscript also are described as follows:

Page 12, line 1 - 5: When the altitude increases to 10 km, the oxalic acid-catalyzed reaction is just 2 orders of magnitude slower than water-catalyzed reaction. At 12 km altitude, the water-catalyzed hydration reaction is approximately 10 times faster than the oxalic acid-catalyzed SO₃ hydration. To sum up, the comparison of relative rate shows that, in the upper troposphere, the oxalic acid can play a

significant role in enhancing SO₃ hydration to H₂SO₄.

We also put the changed tables as follows:

The old Table 1:

Table 1. Rate constants (in cm³ molecule⁻¹ s⁻¹) of SO₃ hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k _{w1}	1.51×10 ⁻¹²	2.01×10 ⁻¹²	2.99×10 ⁻¹²	4.62×10 ⁻¹²	7.44×10 ⁻¹²	1.27×10 ⁻¹¹	2.26×10 ⁻¹¹	3.13×10 ⁻¹¹
k _{w2}	3.12×10 ⁻¹²	5.06×10 ⁻¹²	9.95×10 ⁻¹²	2.08×10 ⁻¹¹	4.71×10 ⁻¹¹	1.16×10 ⁻¹⁰	3.15×10 ⁻¹⁰	5.46×10 ⁻¹⁰
k _{cTt1}	5.87×10 ⁻⁸	1.26×10 ⁻⁷	3.67×10 ⁻⁷	1.19×10 ⁻⁶	4.39×10 ⁻⁶	1.86×10 ⁻⁵	9.33×10 ⁻⁵	2.29×10 ⁻⁴
k _{cTt2}	1.05×10 ⁻⁹	1.94×10 ⁻⁹	4.60×10 ⁻⁹	1.19×10 ⁻⁸	3.40×10 ⁻⁸	1.09×10 ⁻⁷	4.02×10 ⁻⁷	8.27×10 ⁻⁷
k _{tTt1}	1.99×10 ⁻⁶	4.84×10 ⁻⁶	1.69×10 ⁻⁵	6.70×10 ⁻⁵	3.07×10 ⁻⁴	1.66×10 ⁻³	1.10×10 ⁻²	3.12×10 ⁻²
k _{tTt2}	5.81×10 ⁻⁸	1.24×10 ⁻⁷	3.60×10 ⁻⁷	1.16×10 ⁻⁶	4.26×10 ⁻⁶	1.80×10 ⁻⁵	8.96×10 ⁻⁵	2.19×10 ⁻⁴
k _{tCt1}	3.10×10 ⁻⁶	7.83×10 ⁻⁶	2.88×10 ⁻⁵	1.21×10 ⁻⁴	5.88×10 ⁻⁴	3.40×10 ⁻³	2.42×10 ⁻²	7.18×10 ⁻²
k _{tCt2}	7.77×10 ⁻⁸	1.70×10 ⁻⁷	5.13×10 ⁻⁷	1.73×10 ⁻⁶	6.58×10 ⁻⁶	2.91×10 ⁻⁵	1.53×10 ⁻⁴	3.85×10 ⁻⁴
k _{cCt1}	1.02×10 ⁻⁵	2.65×10 ⁻⁵	1.02×10 ⁻⁴	4.49×10 ⁻⁴	2.32×10 ⁻³	1.43×10 ⁻²	1.09×10 ⁻¹	3.35×10 ⁻¹
k _{cCt2}	5.48×10 ⁻⁸	1.16×10 ⁻⁷	3.37×10 ⁻⁷	1.08×10 ⁻⁶	3.94×10 ⁻⁶	1.65×10 ⁻⁵	8.21×10 ⁻⁵	1.99×10 ⁻⁴

The new Table 1:

Table 1. Rate constants (in cm⁶ molecule⁻² s⁻¹) of SO₃ hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k _{w1} (k _{w2})	4.21×10 ⁻³¹	9.74×10 ⁻³¹	3.19×10 ⁻³⁰	1.18×10 ⁻²⁹	4.94×10 ⁻²⁹	2.45×10 ⁻²⁸	1.46×10 ⁻²⁷	3.92×10 ⁻²⁷
k _{cTt1} (k _{cTt2})	6.45×10 ⁻²⁸	2.16×10 ⁻²⁷	1.18×10 ⁻²⁶	7.67×10 ⁻²⁶	6.09×10 ⁻²⁵	6.09×10 ⁻²⁴	8.00×10 ⁻²³	3.35×10 ⁻²²
k _{tTt1} (k _{tTt2})	2.32×10 ⁻²⁶	8.79×10 ⁻²⁶	5.81×10 ⁻²⁵	4.63×10 ⁻²⁴	4.56×10 ⁻²³	5.86×10 ⁻²²	1.02×10 ⁻²⁰	4.97×10 ⁻²⁰
k _{tCt1} (k _{tCt2})	4.08×10 ⁻²⁶	1.62×10 ⁻²⁵	1.13×10 ⁻²⁴	9.55×10 ⁻²⁴	1.01×10 ⁻²²	1.40×10 ⁻²¹	2.64×10 ⁻²⁰	1.35×10 ⁻¹⁹
k _{cCt1} (k _{cCt2})	1.39×10 ⁻²⁵	5.70×10 ⁻²⁵	4.17×10 ⁻²⁴	3.71×10 ⁻²³	4.17×10 ⁻²²	6.15×10 ⁻²¹	1.24×10 ⁻¹⁹	6.61×10 ⁻¹⁹

The old Table 2:

Table 2. Relative rate constants of oxalic acid catalyzed SO₃ hydration with respect to water catalyzed SO₃ hydration at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k _{cTt1} /k _{w1}	3.88×10 ⁴	6.27×10 ⁴	1.23×10 ⁵	2.58×10 ⁵	5.90×10 ⁵	1.47×10 ⁶	4.12×10 ⁶	7.30×10 ⁶

k_{cTt2}/k_{w2}	3.36×10^2	3.83×10^2	4.63×10^2	5.70×10^2	7.22×10^2	9.41×10^2	1.28×10^3	1.52×10^3
k_{tTt1}/k_{w1}	1.31×10^6	2.41×10^6	5.65×10^6	1.45×10^7	4.13×10^7	1.31×10^8	4.84×10^8	9.95×10^8
k_{tTt2}/k_{w2}	1.86×10^4	2.45×10^4	3.62×10^4	5.58×10^4	9.04×10^4	1.55×10^5	2.85×10^5	4.00×10^5
k_{cCt1}/k_{w1}	2.05×10^6	3.90×10^6	9.62×10^6	2.61×10^7	7.91×10^7	2.69×10^8	1.07×10^9	2.29×10^9
k_{cCt2}/k_{w2}	2.49×10^4	3.37×10^4	5.16×10^4	8.26×10^4	1.40×10^5	2.51×10^5	4.88×10^5	7.06×10^5
k_{cCt1}/k_{w1}	6.73×10^6	1.32×10^7	3.42×10^7	9.72×10^7	3.12×10^8	1.13×10^9	4.80×10^9	1.07×10^{10}
k_{cCt2}/k_{w2}	1.76×10^4	2.30×10^4	3.39×10^4	5.19×10^4	8.37×10^4	1.43×10^5	2.61×10^5	3.65×10^5

The new Table 2:

Table 2. Relative rate constants of oxalic acid catalyzed SO₃ hydration with respect to water catalyzed SO₃ hydration at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k_{cTt1}/k_{w1}	1.53×10^3	2.21×10^3	3.70×10^3	6.52×10^3	1.23×10^4	2.49×10^4	5.49×10^4	8.54×10^4
k_{tTt1}/k_{w1}	5.50×10^4	9.03×10^4	1.82×10^5	3.94×10^5	9.24×10^5	2.40×10^6	6.98×10^6	1.27×10^7
k_{tCt1}/k_{w1}	9.70×10^4	1.66×10^5	3.53×10^5	8.12×10^5	2.05×10^6	5.73×10^6	1.81×10^7	3.45×10^7
k_{cCt1}/k_{w1}	3.31×10^5	5.86×10^5	1.31×10^6	3.16×10^6	8.44×10^6	2.51×10^7	8.54×10^7	1.69×10^8

The old Table 5:

Table 5. Relative rate of SO₃ hydration reaction catalyzed by oxalic acid and by water at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
$v_{SO_3 \cdots H_2O+OA} / v_{SO_3 \cdots H_2O}$	8.62×10^{-5}	3.54×10^{-4}	1.00×10^{-3}	4.08×10^{-3}	1.82×10^{-2}	9.74×10^{-2}	1.12	6.78

^aThe rate $v_{SO_3 \cdots H_2O+OA}$ represents the sum of reaction rate for SO₃⋯H₂O complex with four oxalic acid conformers (cTt, tTt, tCt, cCt). The rate ($v_{SO_3 \cdots H_2O+cTt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+tTt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+tCt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+cCt}/v_{SO_3 \cdots H_2O+H_2O}$) are shown in Table S10.

The new Table 5:

Table 5. Relative rate of SO₃ hydration reaction catalyzed by oxalic acid and by water at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
v_{OA1}/v_{w1}	3.87×10^{-6}	1.43×10^{-5}	3.47×10^{-5}	1.20×10^{-4}	4.43×10^{-4}	1.95×10^{-3}	1.80×10^{-2}	9.53×10^{-2}

^aThe rate v_{OA1} represents the sum of reaction rate for Reaction X1 (X=cTt, tTt, tCt, cCt). The rate (v_{cTt1}/v_{w1} , v_{tTt1}/v_{w1} , v_{tCt1}/v_{w1} , v_{cCt1}/v_{w1}) are shown in Table S10.

3. In Section 3.1: it is better to compare the results with previous studies to enrich the text.

Reply: Thank you for your advice. We have added the discussion about the comparison of the results with literatures. The added contents are shown in the revised manuscript (Page 7, line 8 - 14), which also are put below:

Page 7, line 9 - 13: Moreover, the binding energy of water dimer is consistent with its experimental value of $3.15 \pm 0.03 \text{ kcal mol}^{-1}$ (Rocher-Casterline et al., 2011), and with theoretical results of 2.90 (Torrent-Sucarrat et al., 2012), 2.97 (Long et al., 2013), 3.14 (Hazra and Sinha, 2011) and 3.30 kcal mol⁻¹ (Klopper et al., 2000). In SO₃⋯H₂O complex, the binding energy of 7.38 kcal mol⁻¹ in our paper agrees with that from theoretical estimates in the literature: 7.60 (Torrent-Sucarrat et al., 2012), 7.42 (Long et al., 2013), 7.25 (Hazra and Sinha, 2011) and 7.77 kcal mol⁻¹ (Long et al., 2012).

Page 7, line 15 - 16: The RC1 has the binding energy of 14.12 kcal mol⁻¹ relative to SO₃+H₂O⋯H₂O, which is in accord with 13.60 (Torrent-Sucarrat et al., 2012) and 13.76 kcal mol⁻¹ (Long et al., 2013).

Minor comments:

1. Page1, line 12(Abtract), "can involve in" should be "can be involved in".

Reply: Thank you for pointing out our mistake. We have corrected this error. The corrected content can be seen from Abstract (Page 1, line 13), which also is shown as follows:

Some atmospheric species can be involved in and facilitate the reaction.

2. Page1, line 16 (Abstract), "the rate of SO3 hydration" should be "the rates of SO3 hydration".

Reply: We have corrected this error in the revised manuscript (Page 1, line 16). The new content is listed below:

Compared with the rates of SO₃ hydration reaction catalyzed by oxalic acid and water, it can be

found that, in the upper troposphere, the oxalic acid-catalyzed SO₃ hydration can play an important role in promoting the SO₃ hydration.

3. Page 2, line 5: is it better to change the second "can" to "thus"?

Reply: We have corrected this error in the revised manuscript (Page 2, line 5). The new content is listed below:

These atmospheric HAT reactions display a main feature that two-point hydrogen bond can occur and thus facilitate hydrogen atom transfer

4. Page 2, line 11: "firstly is" should be "is firstly".

Reply: We have corrected this error in the revised manuscript (Page 2, line 11). The new content is listed below:

For the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, the pre-reactive $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex is firstly formed, and the complex is then rearranged to produce H_2SO_4 , which was proposed by Castleman et al (Holland and Castleman, 1978; Hofmann-Sievert and Castleman, 1984).

5. Page 2, line 11: "rearrange" should be "rearranges".

Reply: We have corrected this error in the revised manuscript (Page 2, line 11). The new content is listed below:

For the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, the pre-reactive $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex is firstly formed, and the complex is then rearranged to produce H_2SO_4 , which was proposed by Castleman et al (Holland and Castleman, 1978; Hofmann-Sievert and Castleman, 1984).

6. Page 2, line 14: "takes" should be "take".

Reply: We have corrected this error in the revised manuscript (Page 2, line 13). The new content is listed below:

But the subsequent research found that this hydration reaction involving a single water molecule cannot take place in the atmosphere due to high energy barrier.

7. Page 2, line 17: "reduce" should be "reduces"

Reply: We have corrected this error in the revised manuscript (Page 2, line 17). The new content is listed below:

The promoting effect can be mainly attributed to the formation of the two-point hydrogen bond, which reduces the ring strain...

8. Page 3, line 15: "for" should be "of".

Reply: We have corrected this error in the revised manuscript (Page 3, line 17). The new content is listed below:

The rate constants of oxalic acid-catalyzed SO_3 hydration were calculated using the kinetics analysis, and compared with that of water-catalyzed hydration reaction.

9. Page 3, line 17: "... the hydration of SO_3 in the second water ..." should be "... the hydration of SO_3 with the second water ...".

Reply: We have corrected this error in the revised manuscript (Page 3, line 19). The new content is listed below:

...we evaluated the importance of the hydration process involving the oxalic acid relative to the hydration of SO_3 with the second water as a catalyst to form sulfuric acid

10. Page 3, line 20: "reactant, complex, transition state" should be "reactants, complexes, transition states".

Reply: We have corrected this error in the revised manuscript (Page 3, line 22). The new content is listed below:

The geometric structures, including all reactants, complexes, transition states and products, were

optimized using M06-2X method (Zhao and Truhlar, 2008) with 6-311++G(3df,3pd) basis set.

11. Page 4, lines 9-10: "..., the electronic energies based on the ..., while the partition functions obtained from ..." should be "..., the electronic energies were based on the ..., while the partition functions were obtained from ...".

Reply: We have corrected this error in the revised manuscript (Page 4, line 11 - 12). The new content is listed below:

In the kinetics analysis, the electronic energies were based on the CCSD(T)/cc-pV(T+d)Z level of theory, while the partition functions were obtained from the M06-2X/6-311++G(3df,3pd) level of theory.

12. Page 4, line 14: "..., it can conclude that the ..." should be "..., it can be concluded that the ...".

Reply: We have corrected this error in the revised manuscript (Page 4, line 16). The new content is listed below:

Base on the discussion in this paper, it can be concluded that the SO₃ hydration reactions begin with the formation of pre-reactive complex...

13. Page 5: "The corresponding rate constants are that" should be "The corresponding reaction rates are that".

Reply: We have corrected this error in the revised manuscript (Page 5, line 7). The new content is listed below:

The corresponding rates are that: ...

14. Page 6, line 10: "react" should be "reacts".

Reply: We have corrected this error in the revised manuscript (Page 7, line 2). The new content is listed below:

One is that water dimer reacts with SO_3 to obtain pre-reactive complex, then this complex is rearranged to form $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex (channel 1); the other begins with the reaction of $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex with water, the following rearrangement is the same as the channel 1 (channel 2).

15. Page 6, line 11: "rearrange" should be "rearranges" and "begin" should be "begins".

Reply: We have corrected this error in the revised manuscript (Page 7, line 3). The new content is listed below:

One is that water dimer reacts with SO_3 to obtain pre-reactive complex, then this complex is rearranged to form $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex (channel 1); the other begins with the reaction of $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex with water, the following rearrangement is the same as the channel 1 (channel 2).

16. Page 7, line 10: "Table S2-S5" should be "Tables S2-S5".

Reply: We have corrected this error in the revised manuscript (Page 8, line 4). The new content is listed below:

Energies, enthalpies and free energies of all relevant species for oxalic acid catalyzed hydration of SO_3 are summarized in Supplement (Tables S2 - S5).

17. Page 10, line 23: is it better to change "real" to "potential".

Reply: We have corrected this error in the revised manuscript (Page 12, line 15). The new content is listed below:

The main conclusion of this work is that oxalic acid, the most abundant dicarboxylic acid in the atmosphere, has the remarkable ability to catalyze SO_3 hydration to H_2SO_4 , and has the potential impact on the H_2SO_4 formation in the atmosphere.

18. Page 11, line 3: is it better to change "The energy barrier of hydration reaction of SO_3 is about or below 1 kcal mol⁻¹" to "Other conformers can catalyze the hydration reaction and the corresponding energy barrier is a little higher or less than 1 kcal mol⁻¹".

Reply: Thank you for your advice. We have changed this sentence in the revised manuscript (Page 12, line 20). We also put it below:

Other conformers can catalyze the hydration reaction and the corresponding energy barrier is a little higher or less than 1 kcal mol^{-1} .

19. Page 11, line 4: add "that" after "signify".

Reply: We have corrected this error in the revised manuscript and changed the word "signify" to "demonstrate" (Page 12, line 21). The new content is listed below:

The results demonstrate that oxalic acid has the higher catalytic ability than water for SO_3 hydration to form H_2SO_4 .

20. Page 11, line 5: add "from the view of barrier" after " H_2SO_4 ".

Reply: Thank you for your advice. We combined the sentence with the previous sentence into a new sentence, and mentioned the two factors (rate constant and concentration). Because the rate constant contains the meaning from the view of barrier, we did not add the content. The new sentence is shown as follows:

Page 13, line 2 - 3: Based on the two factors, our calculation shows that, in the upper troposphere, the oxalic acid can play an important role in SO_3 hydration to form H_2SO_4 .

21. Page 22, the caption of Figure 4. Please add the unit of hydrogen bond length.

Reply: Thank you for your advice. We have added the unit in the caption of Figure 4. The new content is listed below:

Figure 4. Optimized M06-2X/6-311++G(3df,3pd) structures of reactant complexes, pre-reactive complexes, transition states and post-reactive complexes for the oxalic acid-catalyzed SO_3 hydration reaction (distance unit: angstrom).